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1/1 ページ

Exhibit**PATENT ABSTRACTS OF JAPAN**

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(54) PRODUCTION OF AROMATIC CARBONIC ACID ESTER**(57)Abstract:**

PURPOSE: To obtain a method for producing a carbonic acid ester by transesterification of an aromatic hydroxy compound with a dialiphatic carbonic acid ester or an aliphatic aromatic carbonic acid ester.

CONSTITUTION: The transesterification of an aromatic hydroxy compound with a dialiphatic carbonic acid ester or an aliphatic aromatic carbonic acid ester is carried out in the presence of at least one selected from a yttrium compound and a thallium compound as a catalyst to produce the objective aromatic carboxylic acid ester. This aromatic carbonic acid ester can be obtained with higher activity at a higher rate of reaction in higher yield than those of a conventional method.

JP,05-331108,A [CLAIMS]

1/1 ページ

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CLAIMS

[Claim(s)]

[Claim 1]The ester exchange reaction of an aromatic hydroxy compound, JI aliphatic carbonic ester, or aliphatic series and aromatic carbonate is carried out, A manufacturing method of aromatic carbonate using as a catalyst at least one sort which it was chosen from an yttrium compound and a thallium compound, and was given in manufacturing aliphatic series and aromatic carbonate, JI aromatic carbonate, or these mixtures.

[Claim 2]A way according to claim 1 a catalyst is at least one sort selected from a yttrium alkoxide, yttrium phenoxide, a yttrium chloride, yttrium acetate, yttrium acetylacetonato, thallium acetylacetonato, thallium oxide, and thallium acetate.

[Claim 3]A way according to claim 1 an aromatic hydroxy compound is phenol.

[Claim 4]A way according to claim 1 JI aliphatic carbonic ester is dimethyl carbonate.

[Translation done.]

JP,05-331108,A [DETAILED DESCRIPTION]

1/4 ページ

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacturing method of aromatic carbonate. It is related with the method of manufacturing aliphatic series and aromatic carbonate, JI aromatic carbonate, or these mixtures, under a detailed existence of a specific catalyst by an ester exchange reaction with an aromatic hydroxy compound, JI aliphatic carbonic ester, or aliphatic series and aromatic carbonate. Aromatic carbonate is a compound useful for uses, such as an aromatic polycarbonate raw material and an isocyanate intermediate.

[0002]

[Description of the Prior Art] Aromatic carbonate is conventionally manufactured by the reaction of an aromatic hydroxy compound and phosgene. However, phosgene's being deadly poison nature and the corrosiveness of a device are high, and also since a lot of alkali is required in order to neutralize the hydrogen chloride which carries out a byproduction, the method which does not use phosgene is demanded, and some trials have been made. For example, the method of carbonylating an aromatic hydroxy compound and carbon monoxide oxidatively in a raw material is proposed, for example, JP,56-38143,B, JP,56-38144,B, JP,56-38145,B, JP,53-68747,A, and JP,54-135743,A, JP,54-135744,A, JP,55-102539,A, JP,2-104564,A, JP,2-142754,A, JP,1-165551,A, etc. are illustrated.

[0003] However, expensive palladium is used for these methods as a main catalyst, and also since they need a co-catalyst, a drier, an oxidizer, etc., they have become the very complicated system of reaction. Moreover, recovery of a catalyst is also difficult and the actual condition is not having resulted in an industrial level in respect of yield and reaction velocity.

[0004] As manufacturing methods other than the above, the ester exchange reaction of an aromatic hydroxy compound and aliphatic carbonic ester is known. for example, the method of making the Lewis acids a catalyst in JP,56-42577,B — JP,60-173016,A **** — the method of making the mixture of Lewis acid and proton acid a catalyst is shown. However, also when corrosiveness is strong, and there is a problem in industrial operation and also it is any, a reaction takes the long time of 24 hours to these acids from 5 hours, and, moreover, their yield is not enough, either. In JP,54-48733,A, although the method of making a tin compound a catalyst is shown, in spite of having applied the reaction time of no less than 30 hours according to the statement of a gazette, sufficient yield is not obtained. JP,60-169444,A **** — although the tin compound of polymer nature is used as a catalyst, preparation is complicated, and also since this catalyst has steam pressure, it has a fault of difficulty in separate recovery with output. further — JP,57-176932,A **** — in spite of showing the method of making a lead compound a catalyst and using a lot of catalysts, too sufficient result is not obtained.

[0005] In addition, although JP,56-25138,A is shown the method of making a catalyst an alkaline metal and an alkaline earth metal compound, as for these catalysts, the top where labile is low has many byproductions of an ether compound. Although the method of making a catalyst Sc, Cr, Mo, W, Mn, Au, Ga, In, Bi, Te, and a lanthanoids compound is shown in JP,1-265064,A, labile is low and also these are not suitable for use with them which has many byproductions of an ether compound, either. [actual]

[0006]

[Problem(s) to be Solved by the Invention] As described above, the catalyst currently used

conventionally should not yet be satisfied from industrial standpoints — in any case, the yield of an objective product is low, and it is not enough in respect of reaction velocity, and further, recovery of a catalyst or separation with an objective product is difficult, and there is. In view of the problem of accepting to the catalyst of these former, this invention does not have the restrictions on device construction material, is high reaction velocity and is with high yield to provide the catalyst which can manufacture aromatic carbonate.

[0007]

[Means for Solving the Problem]As a result of repeating research wholeheartedly that the above-mentioned problem should be solved, this invention persons find out an outstanding catalyst and came to complete this invention.

[0008]Namely, this invention carries out the ester exchange reaction of an aromatic hydroxy compound, JI aliphatic carbonic ester, or aliphatic series and aromatic carbonate. In manufacturing aliphatic series and aromatic carbonate, JI aromatic carbonate, or these mixtures, it is the method of using at least one sort selected from an yttrium compound and a thallium compound as a catalyst. There are no exceptional restrictions on device construction material by this method, and manufacture of aromatic carbonate is possible at high yield and a high generation rate.

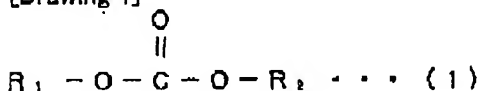
[0009]As a catalyst used for this invention, at least one sort of compounds selected from an yttrium compound and a thallium compound are used. As these compounds, yttrium or thallium should be just contained as an ingredient. For example, although those oxides, a halogenide, a nitric acid ghost, a sulfuration thing, a phosphorylation thing, hydroxide, a carboxylic acid compound, an acetylacetonato compound, a carbonate compound, an alkoxide compound, a phenoxide compound, etc. are illustrated, As a desirable catalyst, a yttrium alkoxide, yttrium phenoxide, a yttrium chloride, yttrium acetate, yttrium acetylacetonato, thallium acetylacetonato, thallium oxide, and thallium acetate are mentioned especially. These catalysts may be independent or may use two or more together.

[0010]As an aromatic hydroxy compound used for this invention, as long as a hydroxy group has combined with an aromatic ring directly, any may be sufficient. As such an aromatic hydroxy compound, For example, phenol, cresol, a xylene, dimethylphenol, Trimethyl phenol, tetramethyl phenol, ethylphenol, Alkylphenols, such as propylphenol, benzylphenol, and bisphenol A; Phenylphenol, Aryl phenols, such as biphenol; Chlorophenol, bromophenol, Halogenated phenol, such as dichlorophenol and dibromophenol; Methylchlorophenol, Alkyl and halogenation phenols, such as ethylchlorophenol, methylbromophenol, and ethylbromophenol; An anisole, Phenols which alkyl or an aryl group combined through hetero atoms, such as phenoxyphenol and phenylthio phenol, are mentioned (all the possible isomers are also contained in the above-mentioned substance). Also in these, phenol is industrially the most preferred.

[0011]JI aliphatic carbonic ester used for this invention is expressed with a general formula (1).

[0012]

[Drawing 1]



(R₁ and R₂ may be univalent aliphatic hydrocarbon groups among a formula, a different thing may be sufficient also as the same thing, and R₁ and R₂ may be ingredients from which R₁ and R₂ constitute a ring, respectively.)

[0013]As an example of R₁ and R₂, Methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, Alkyl groups, such as octyl, nonyl, decyl, allyl, butenyl, and cyclohexylmethyl; Cyclopropyl, Alicycle fellows groups, such as cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl one; ARARUKIRU groups, such as benzyl, phenethyl, phenylpropyl, phenylbutyl, and methylbenzyl, are mentioned (all the possible isomers are also contained in the above-mentioned group).

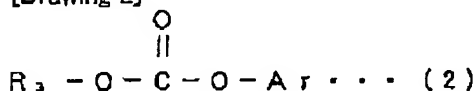
[0014]As an example of JI aliphatic carbonic ester expressed with a general formula (1), Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, Dibutyl carbonate, dipentyl carbonate, dihexyl carbonate, Diheptyl carbonate, dioctyl carbonate, dinonyl carbonate, Didecyl carbonate, diaryl

carbonate, dibutenyl carbonate, dicyclohexyl carbonate, dibenzyl carbonate, ethylene carbonate, etc. are mentioned (a possible isomer is also contained in the above-mentioned compound). In these JI aliphatic carbonic ester, dimethyl carbonate is used most preferably.

[0015]The aliphatic series and aromatic carbonic acid acid ester which is the raw material or output in this invention are expressed with a general formula (2).

[0016]

[Drawing 2]



(It is R_3 and a ** univalent aliphatic hydrocarbon group among a formula, and Ar expresses a univalent aromatic group.)

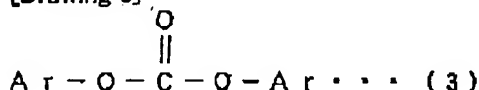
[0017]The example of R_3 is the same as R_1 of a general formula (1), or R_2 , and as an example of Ar, Phenyl, tolyl, xylyl, trimethyl phenyl, tetramethyl phenyl, Ethylphenyl, propylphenyl, butylphenyl, diethylphenyl, A phenyl group and alkylphenyl groups, such as methylethyl phenyl, pentylphenyl, hexylphenyl, and cyclohexylphenyl; Methoxyphenyl, Alkoxyphenyl groups, such as ethoxyphenyl and butoxyphenyl; Chlorophenyl, Halogenation phenyl groups, such as bromophenyl, dichlorophenyl, and dibromophenyl; Methyl chlorophenyl, Alkyl and halogenation phenyl groups, such as ethyl chlorophenyl, methylbromophenyl, and ethylbromophenyl, etc. are mentioned (all the possible isomers are also contained in the above-mentioned group).

[0018]As an example of aliphatic series and aromatic carbonate expressed with a general formula (2), Methylphenyl carbonate, ethylphenyl carbonate, propylphenyl carbonate, Butylphenyl carbonate, benzylphenyl carbonate, cyclohexylphenyl carbonate, methyl tolyl carbonate, ethyl tolyl carbonate, methylxylyl carbonate, etc. are mentioned (all the possible isomers are also contained in the above-mentioned compound). In these aliphatic series and aromatic carbonate, methylphenyl carbonate is the most important.

[0019]The JI aromatic carbonate which is the output of this invention is expressed with a general formula (3).

[0020]

[Drawing 3]



(The inside of a formula and Ar are the same as said formula (2)). As an example of a general formula (3), diphenyl carbonate, JITORIRU carbonate, phenyl tolyl carbonate, JI (ethylphenyl) carbonate, etc. are mentioned. In it, the industrial most important JI aromatic carbonate is diphenyl carbonate.

[0021]Although the amount of the catalyst used in this invention is a quantity generally called catalyst amount and there is no restriction in particular, it is usually used in 0.001wt% to 30wt% of the range to a raw material.

[0022]The raw material mole ratio of an aromatic hydroxy compound, and JI aliphatic carbonic ester, or aliphatic series and aromatic carbonate is performed to 1 mol of aromatic hydroxy compounds in the range JI aliphatic carbonic ester, or whose aliphatic series and aromatic carbonate is 0.01-20 mol.

[0023]In [wide] 30-350 **, although the reaction temperature in this invention is possible, it is preferably performed in 90-280 **. Although the reaction is possible also on condition of any of ordinary pressure, application of pressure, and decompression, it is more desirable to perform it by a pressurizing condition, when performing the boiling point of a raw material at the temperature which exceeds greatly. Although reaction time changes with other reaction conditions, it is usually preferably performed in 30 minutes - 6 hours for several minutes - tens hours.

[0024]As for the reaction in this invention, it is preferred to carry out removing the alcohol which carries out a byproduction out of the system of reaction in order to shift a balance to the output side.

JP.05-331108,A [DETAILED DESCRIPTION]

4/4 ページ

In that case, the entrainer of alcohol may be added to the system of reaction. In order to use an inertness solvent to a reaction or to remove byproduction alcohol efficiently, it is also possible to introduce inactive gas. Hereafter, although an example is given and the method of this invention is explained, this invention is not limited to these examples.

[0025]

[Example]

In the 100-ml glass flask equipped with the VIGURYUU fractionating column of 120 cm of examples, 0.15 g of yttrium TORIISO propoxide was put in as the phenol 42.35g (0.45 mol), 13.51g (0.15 mol) of dimethyl carbonate (DMC), and a catalyst, and temperature up was performed under stirring. 3 hours was required, reaction temperature was gradually raised from 145 ** to 165 **, and the methanol which carries out a byproduction was distilled off in the meantime. As a result of gas chromatography's analyzing reaction mixture, in methylphenyl carbonate (MPC), 6.02 g and diphenyl carbonate (DPC) were generating 0.80g. DPC is [this] equivalent to the yield of 2.5% for MPC 26.3% on a DMC standard. The anisole was below the detection limit.

[0026] It replaced with Example 2 - 7 yttrium TORIISO propoxide, and reacted by the same method as Example 1 except having used various yttrium compounds shown in a table.

[0027]

[Table 1]

Table 1 Yield of DMC standard (%)

Example NO ** Intermediation Seed MPC DPC anisole.		
Example 2	yttrium ethoxide	24.7, 2.40, 0.3
Example 3	yttrium n-butoxide	23.3, 2.1, 0.0
Example 4	yttrium phenoxide	25.3, 2.5, 0.0
Example 5	yttrium chloride	18.6, 1.3, 0.0
Example 6	yttrium acetate	21.5, 1.3, 0.0
Example 7	yttrium acetylacetonate	21.7, 2.2, 0.0

[0028] It replaced with Example 8 - 10 yttrium TORIISO propoxide, and the reaction was carried out for various thallium compounds to the catalyst by the same method as Example 1. A result is shown in Table 2.

(Following space)

[0029]

[Table 2]

Table 2 Yield of DMC standard (%)

Example NO ** Intermediation Seed MPC DPC anisole example 8		
Example 9	thallium acetylacetonate	15.4, 2.2, 0.0
Example 10	thallium oxide	18.0, 2.2, 0.0

[0030] 0.71 g of yttrium TORIISO propoxide was put into the autoclave made from 11500 ml of examples titanium as the phenol 150.58g (1.60 mol), DMC 48.04g (0.53 mol), and a catalyst. After 10.0 kg/cm² of nitrogen replaced the inside of a 2 times reactor, it was filled up with nitrogen to 4.0 kg/cm². Under stirring, temperature up was performed and it could be 250 **. The pressure in a reactor always maintained 4.0 kg/cm² with the constant-pressure machine. The reaction was continued at 250 ** for 3 hours, and the low-boiling ingredient was distilled off via the capacitor in the meantime. As a result of gas chromatography's analyzing reaction mixture, in MPC, 12.54 g generated and, in DPC, 23.05 g and an anisole were generating 0.15g. A DMC standard and MPC are equivalent to 15.5%, DPC is equivalent to 20.3%, and an anisole is [this] equivalent to the yield of 0.3%.

[0031] It replaced with example 12 yttrium TORIISO propoxide, and thallium oxide was reacted to the catalyst by the same method as Example 12. As a result, in MPC, 9.75 g generated and, in DPC, 18.74 g and an anisole were generating 0.10g. A DMC standard and MPC are equivalent to 12.1%, DPC is equivalent to 16.5%, and an anisole is [this] equivalent to the yield of 0.2%.

[0032]

[Effect of the Invention] According to this invention, reaction velocity is high, moreover, compared with the conventional catalyst, it is high activity, and it is [there is little generation of a by-product it can obtain the aromatic carbonate which is an objective product with high yield, and] an industrial very significant method.

[Translation done.]